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VOL. XXI JUNE, 1905 NO. 2

JOURNAL

OF THE

Elisha Mitchell Scientific Society

ISSUED QUARTERLY

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Journal of the Elisha Mitchell Scientific Society—Quarterly. Price $3.00 per year; single numbers 50 cents. Most numbers of former volumes can be supplied. Direct all correspondence to the Editors, at University of North Carolina, Chapel Hill, N. C.

JOURNAL

OF THE

ELISHA MITCHELL SCIENTIFIC SOCIETY.

JUNE, 1905

VOL. XXI NO. 2

PROCEEDINGS OF THE FOURTH ANNUAL MEETING

OF THE

NORTH CAROLINA ACADEMY OF SCIENCE

HELD AT

A. & M. COLLEGE, RALEIGH, N. C., MAY 12-13, 1905.

MAY 13, 1905.

Meeting called to order by President Stevens at 8:30 P. M., but adjourned for informal conference during which a number of matters were discussed.

MAY 14, 1905.

Meeting called to order at 10 A. M. by President Stevens, who at once appointed Messrs. C. S. Brimley and W. C. Coker as Nominating Committee.

Upon proper presentation of names, Messrs. G. M. Bentley, of the North Carolina Department of Agriculture, at Raleigh, and J. G. Boomhour, of the Baptist Female University also at Raleigh, were elected members.

The Academy then proceeded to the presentation of papers, which were given in the following order:

[Issued September 20th, 1905.]

1. ABNORMALITIES IN THE EMBRYO-SAC OF LILLIUM TIGRINUM: *F. L. Stevens.*

Three abnormalities were noted. In one case the nucleus at the micropilar end of the embryo sac was undergoing constriction while in the spirem stage without any sign of spindle formation. In another case five nuclei, three of these cut off by walls, were in the antipodal end of the embryo sac. Another slide exhibited an excessively long nucleus in the micropilar end of the embryo sac. No explanation was offered. Slides showing the structures referred to were exhibited to the Academy.

2. NOTES ON THE FOOD AND FEEDING-HABITS OF SOME NORTH AMERICAN REPTILES: *C. S. Brimley.*

Personal observation describing how a snake swallows an animal or egg apparently too large for such process. Mentions the food upon which snakes, lizards and turtles have been observed to feed. Describes how a king snake kills another snake.

3. ON THE RECORDED DISTRIBUTION OF CERTAIN INJURIOUS INSECTS IN NORTH CAROLINA: *F. Sherman, Jr.*

Attention was called to the value of positive data concerning the distribution of injurious insects determining the probable results of sporadic out-breaks and informing the prospective planter or orchardist of the pests to be encountered in any particular locality. The Division of Entomology of the North Carolina Department of Agriculture has been keeping accurate records of all reported insect outbreaks for over four years. Some species appear to be generally distributed, others so meagrely recorded as to furnish no conclusions as yet, while still others show fairly well-defined limits.

Notes and maps to illustrate distribution were given as follows:—*Chinch Bug* occurs probably throughout the state east of the mountains, but most destructive in the piedmont section. *Corn Bill-beetle*, probably occurs throughout eastern half of the state, but is chiefly destructive along rivers and streams subject to overflow in the eastern section. *Oyster-shell Bark-louse*, probably occurs throughout the moun-

tain and piedmont sections, but chiefly destructive in the mountains. *San Jose Scale*, occurs in various localities in all sections of the state and has been spread largely by shipment of infested plants. *Strawberry Weevil*, occurs in the strawberry-growing region in the southeast with questionable records for the counties of Wilson, Richmond, and Buncombe.

4. A NEW APPLE-TREE DISEASE. *F. L. Stevens.*

A disease designated as scurf was described. It is an infection of the bark on young twigs, causing a wrinkling and cracking, somewhat resembling the San José scale in appearance. The fungus causing this disease was exhibited in pure plate and tub culture before the Academy. Inoculation experiments are in progress, and a canvas of the state is being made in order to determine the extent of distribution and seriousness of the disease.

Remainder of the papers were withheld to be read at the Joint Session with the North Carolina Section of the American Chemical Society.

The Academy then proceeded with the business of the regular business meeting and upon report of the nominating committee and by ballot the following officers for the next year were elected:

President, PROF. JNO. F. LANNEAU, Wake Forest.

Vice-President, DR. TAIT BUTLER, Dept. Agr. Raleigh.

Secretary-Treasurer, DR. F. L. STEVENS, A. & M. College, West Raleigh.

Executive Committee:—PROF. JNO. F. LANNEAU, *ex officio*, DR. F. L. STEVENS, PROF. COLLIER COBB, Chapel Hill; MR. H. H. BRIMLEY, Dept. Agr., Raleigh; MR. F. SHERMAN, JR., Dept. Agr., Raleigh.

At this point the members of the Chemical Society entered and the Academy proceeded to the business of the joint session, at which the following papers were presented:

1. THE SCIENCE OF PLANT PATHOLOGY, (Presidential Address of President) *F. L. Stevens for the Academy*. (Appears in full in this issue.)

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2. A NEW COLOR REACTION FOR LIGNOCELLULOSE: *A. S. Wheeler.*

3. PHYSICS OF SHOOTING STARS: *Jno. F. Lanneau.*

4. CORROSION OF IRON: *R. O. E. Davis.*

5. CONDENSED FORM OF FAT EXTRACTOR AND ETHER RECOVERER: *J. M. Pickel.*

6. BUTTERFLIES OF RALEIGH, N. C.: *C. S. Brimley.*

   In this paper the number of species belonging to each of the families of butterflies was enumerated. Paper was illustrated by specimens prepared in Riker mounts.

7. A PHARMACIST'S VIEW OF PATENT MEDICINES: (summarized only) *E. V. Howell.*

At the conclusion of this program President Williams of the Chemical Section announced the adjournment of both bodies to Giersch's Café where a lunch was tendered the visitors by the Raleigh members of both organizations.

FRANKLIN SHERMAN, JR.,
Retiring Secretary.

THE SCIENCE OF PLANT PATHOLOGY.*

BY PROFESSOR FRANK LINCOLN STEVENS, PH.D.,
North Carolina College of Agriculture.

From the time men first had interest in plants, knowledge of their imperfections or premature death has existed, without, however, definite conception that the imperfections in question really constitute a condition of disease.

The Bible and the early writings of the Greeks and Romans contain references to what we now recognize as wheat rust, fig blight, insect galls and other of the more strikingly conspicuous plant ailments. Such references are more abundant in the literature of the seventeenth century, and in the latter part of that and the eighteenth century a few papers giving careful descriptions of malformations due to insect invasion appeared. Even the law was invoked to aid in combating the wheat rust in France as early as 1660. Prior to the nineteenth century, however, knowledge of plant diseases can hardly be said to consist of more than mere observation of the fact that such diseases occur, and the little real knowledge that did exist was swamped by rampant superstition.

It is natural that the first attempts to explain imperfections were founded upon climatic and soil relations. Vestigial beliefs prevail to this day throughout the country among the untutored to the effect that the various blights, rusts, rots, mildews, etc., are caused solely by untoward conditions of weather, or the unpropitious position of celestial bodies or some other occult influence.

The significance of one great factor in the production of plant disease, namely the parasitic fungi, remained quite unrecognized until the second decade of the nineteenth cen-

*Reprinted from The Popular Science Monthly, September, 1905.

tury. Fungi had been seen upon the plant and had been described in some detail during the preceding decade, but instead of being recognized as casual agents of disease they were, as was the fate of bacteria in the case of animal diseases, by many regarded as products of disease. Before the study of plant diseases could be scientifically undertaken, the basic facts of plant nutrition were to be discovered, the parasitic habit of the fungi proved, the minute anatomy of the plant disclosed. Epoch-making in the disclosure of these desiderata, which may be said to have given birth to plant pathology as a science in the second decade of the nineteenth century were the investigations of the early Dutch, French, German and English botanists. Like bacteriology, plant pathology is an infant science of the last century, owing its being to the perfection of the microscope.

In the last two decades of the last century, scientific effort concerned itself chiefly with accumulating knowledge concerning fungi and insects. Vast numbers of these were classified, catalogued and described. In other words, the means of diagnosis were perfected and diseases were grouped into natural classes according to their casual agents. Attempts toward the development of methods of treatment by the use of various sprays were more or less effective. Indeed, spraying had been advocated to some slight extent for a century or more as a remedy for insect and other plant diseases. The variety of spraying substances ranged from clay, ashes and cow manure to sulphur, lime, salt, etc. One writer recommended "The applying around the base of the tree; flax, rubbish, sea weed, ashes, lime, sea shells, sea sand, mortar, clay, tanner's bark, leather scraps, etc."—evidently not a homeopathic prescription. The variety of substances recommended raises suspicion that the efficiency of no formula was demonstrated. In 1787 we find the heroic advice, 'just wet the trees infested with lice, then rub flowers of sulphur upon the insects, and it will cause them all to burst.' Some decided progress was, however, made. As early as 1842, a whale

soap was used and retained favor; quassi, hellebore and tobacco were standard insecticides as early as 1855. Sulphur was used for the mildews and bluestone for wheat smut.

The last twenty years of the nineteenth century mark the beginning of a new epoch in plant protection. For this there are three reasons: first, the increased aggressiveness of a certain fungous disease, the grape mildew, in Europe; second, the rapid spread of the potato bug, somewhat pedantically termed the Colorado beetle, and, third, resulting from these two, revolutionary changes in materials and methods for treating plant diseases, both fungous and insect, in the new world and in the old. It is a matter not entirely without interest that the revolution in European methods may be definitely traced to typical American aggressiveness, inasmuch as the activity arousing fungus was of American importation.

In Europe the invasion of the downy mildew of the grape in 1878 was unchecked by the most vigorous fungicides then used. All are familiar with the story of the great benefit conferred upon humanity through the predatory habits of the French boys in the vineyards that produce the famous Bordeaux wines. The rows lying nearest the roadway were sprinkled with verdigris or a mixture of lime and bluestone, to give the impression that the fruit was poisoned. In 1882 Millardet, of the faculty of the sciences, noticed that the vines thus treated held their leaves while others succumbed to the mildew. He ascribed this effect to its proper cause, and conducted carefully systematized experiments, which resulted in giving to the world *bouillie bordelaise*, *Bordelaiser Bruhe*, or Bordeaux mixture, a proved fungicide of great efficiency; one that has not yet been surpassed.

In the new world the extension of the potatoe belt westward connected the eastern potato belt with the region of the native food plant of the familiar potato bug. Finding the potato plant a more abundant and wholesome food than the wild solonaceous plants that it had formerly fed upon, the

potato bug began its eastern migration. In 1859 it was found east of Omaha City, in 1868 it had reached Illinois, in 1870 Ontario, in 1872 New York and in 1874 it was upon the Atlantic seaboard. The potato bug ate ravenously and man was stimulated to new activity in the search for more effective means to overcome insect pests. The use of Paris green and London purple followed as a direct result of this stimulus.

The development of efficient fungicides and insecticides in Europe and America led naturally to the perfection of the machines used in applying these mixtures, and not the least important part played in the development of a practical plant pathology is concerned with the evolution of spraying machines. The first sprayer consisted of a bunch of switches. This was dipped into the spraying mixture which was distributed over the foliage by vigorous shaking. It gave place to an improved spraying broom or brush with hollow handle, the liquid flowing from a reservoir to the brush, from which it was applied to the leaves. Sprayers and pumps followed in turn. Then came the improvement of the nozzle.

We may recognize two periods in the development of plant pathology: the first or embryonic period extending from prehistoric times to the beginning of the truly scientific investigations in the middle of the eighteenth century, and contributing chiefly observations, collections, descriptions; the second or formative period, during which the foundations of the science were laid, the chief factors of it determined, and the chief lines of future progress marked out.

It is in no way my purpose to call attention to the part the Carolinas have played in botany as a science, yet I can not refrain in passing from mentioning that prominent place in the history of American mycology is assured to de Schweinitz, a minister of Salem, N. C., who in 1818 published the first important paper on American fungi; to M. A. Curtis, a tutor in Wilmington, N. C., who in 1830, with Berkeley in

England, described many fungi of the Carolinas; to Ravenal, of South Carolina, the first to publish exsiccati of American fungi, and to Louis Bosc, of South Carolina, who published a descriptive list in 1811.

The embryonic and formative period prepared the way for the third period, beginning about 1885, which may be called the period of growth. It is marked by the development and perfection of the rudimentary principals and discoveries of the preceding periods. It was during this period that the most spectacular conquests were made; that popularization and extension of methods occurred. So great, so numerous, so wonderful were the advances made during the past decade, that we frequently see the statement that little or no progress had been made in plant pathology prior to 1885. The present day student should, however, bear in mind that it was the persistent, arduous, patient work of the preceding years that rendered possible the progress of the closing years of the century.

My denomination of this period as 'the period of growth' indicates the nature of the changes which it inaugurates; growth in every direction and concerning every phase of the subject. There has been growth in the list of plant maladies. New diseases have been discovered by scores, and old diseases have been found to affect new plants, and diseases hitherto insignificant have taken prominent places as dangerous foes. The alteration of the plant constitution by high selection and breeding, the bringing of plants into new climatic or soil relations, the more intensive cultivation, the bringing of a susceptible plant into a region where a parasite is already growing upon one of its botanical relatives, thus exposing it to a possible new foe, are conditions that operate to admit of the evolution of new diseases. The growing of plants in large quantities in solid blocks, rather than sparingly in scattered gardens, brings about a congested condition comparable with the crowding of our cities, and favors

the development of epidemics* by furnishing abundant material for the parasitic organisms to attack, abundant nutriment upon which they may multiply, and abundant opportunity for them to reach new hosts and spread the contagion. With potatoes, for example, raised merely as garden crops, the probability of an epidemic affecting the majority of gardens is not so great as when potatoes are raised in vast fields. A single field crop, once infested, so contaminates the air with spores that other fields are almost sure to become infected. The contagium becomes sufficiently multiplied to break the quarantine, and a general epidemic results. Any factor which tends to increase the occurrence of epidemics may quickly raise a given disease from obscurity to a position of commanding importance. So, too, does the increase in value of hitherto comparatively insignificant crops. The pecan and cranberry are at present objects of particular solicitude by the plant physician.

With the importation of plants from foreign countries and the transportation of plants from one part of the country to another comes the possibility of increased disease transference. Recent years have seen the San José scale spread from the Pacific to the Atlantic; the asparagus rust from the Atlantic to the Pacific; the hollyhock rust has invaded us from Europe; the chrysanthemum rust from the Orient; the watermelon wilt is now moving northward and the peach yellows southward. In nearly all cases where the soil is diseased the affected region is annually enlarging, so that soil diseases a decade ago insignificant in the territory of their occupation are fast assuming control of alarmingly large regions. The growing of plants in larger quantities also increase the amount of germ-bearing refuse to the ultimate end that the very air and soil become germ laden.

Civilization, higher culture and community life, especially

*The use of the word epidemic in relation to plant diseases while etymologically incorrect, seems justified since no other word conveys the desired meaning and the meaning of this word is clear to all.

if it verge upon congestion of population, exacts an inevitable forfeiture by increased mortality. Thus does the list of diseases that comes within the horizon of the practical men enlarge. Wonder, often scepticism, is expressed at the existence of unfamiliar diseases of man, other animals and plants, as though these afflictions were conjured up by the examination of the over zealous practitioner. The increase of affliction is more apparent than real, as it is in the case of appendicitis, which is now recognized, named and cured, consequently, heard of, whereas under the old régime it was not recognized as a distinct disease, therefore it was unheard of, though the patient died. Parallel cases might be cited among the plants.

The work of DeBary on polymorphism among the fungi is being extended. Knowledge of the life histories of various pathogenic fungi is being slowly expanded. Summer forms are connected with winter forms, and thereby the hibernating condition, often the most vulnerable point of attack, exposed. The discovery of heteroecism in the rusts, the alternation from wheat to barberry, from apple to juniper is of classic antiquity in the annals of plant pathology. It emphasized the need of close study of life histories of all parasites. Such study has given abundant fruit, notably in disclosing the relation between the apple cankers and the bitter rot of the apple, and revealing the winter condition of the brown rot of the peach. The lead so fortunately made in the discovery of the Bordeaux mixture has been assiduously prosecuted. The original Bordeaux mixture has been greatly modified, changed, indeed, from a thick paste to a thin solution, and so thoroughly tested in all its modifications, that it has now reached its ultimate perfection. Hundreds of other chemicals, both dry and wet, have been tested as fungicides, with the adoption of a few adapted to special conditions, *e. g.*, sulphur and sulphides for powdery mildews and the ammoniacal copper carbonate for use as the fruit ripens, thus avoiding unsightly spotting. A happy combination of insecticide and

fungicide has been found in the various sulphur washes. There has been very remarkable growth in the perfection of spraying appliances; pumps and dusters of many kinds are upon the market. Particularly is the improvement in nozzles to be noted. Nozzles constructed upon scientific principles, capable of applying the liquid in the form of the finest spray to the tops of the highest trees. In the place of the old hand pump and pail we find barrel pumps on wheels, tanks on wheels with pumps operated by gearing attached to the wheels, and finally for the larger fruit farms and for municipal care of shade trees are multiple pumps driven by steam power.

The treatment of seeds to kill adhering spores has been improved upon in many details. It illustrates especially well the nature of the development during the present epoch of plant pathology. Originally the treatment for wheat smut was based purely upon superstition. Pliny, for example, says that 'if branches of laurel are fixed in the ground the disease will pass from the field into the leaves of the laurel.' Tull in 1730 says that there are but two remedies proposed, brining and changing the seed. The avoidance of certain kinds of manure because of their effect upon the host plant and because they carried the smut spores was also advocated about that time. The scientific demonstration by Brefeld that the plant is susceptible only when very small, gave rise to the thought that by hastening the early growth the period of susceptibility could be shortened, and methods of planting and tilling in accord with that idea were advocated. In addition to cultural methods mechanical treatment of seeds, such as passing the wheat loosely between millstones, violent fanning, etc., were suggested about 1786. The chemical treatment of seeds, says Tull, was accidentally discovered about 1660 by the sinking of a shipload of wheat at Bristol, and afterwards, finding it unfit for breadmaking, it was used for seed wheat. The following harvest in England was very smutty except in the case of this accidentally brined seed,

which made a clean crop. Then followed brining with liming and liming without brining, soaking in lime, arsenic, salt, arsenic and lye, and various other treatments, none of which, however, came into general use. Accident coupled with acumen again aided in hastening a discovery. Provost while attempting to germinate some spores placed some of them in water distilled in a copper vessel. These failed to germinate, though similar spores placed in water which had not touched copper germinated well. Following this lead he and numerous other investigators experimented extensively with copper compounds during succeding years.

Such is the history of the development of a treatment effective for smut of wheat and barley, but not for that of oats. The next marked advance was made by Jensen, a Dane, who in 1887 developed the famous Jensen hot water treatment, a treatment which though requiring considerable accuracy of manipulation was thoroughly effective. This method, if no easier were to be had, was well worth to practical agriculture all that the experiment stations of the world have ever cost. Within only a few years, however, the Jensen treatment was supplanted by the formalin treatment; a treatment so simple, inexpensive and effective that, save for minor improvements of detail, the end seems to have been reached in the search for preventives for the particular diseases to which the method applies.

Growth of knowledge concerning bacterial diseases has occurred, beginning with the pear blight which baffled all horticulture prior to the assertion of its bacterial nature by Professor Burrill. The proof that bacteria can and do cause plant diseases has been definitely adduced, and a large number of such diseases have been recognized upon many plants. Not only from the scientific side have these ailments been studied, but from the practical as well, and preventive and palliative measures have in many instances been found.

The soil is often spoken of as the living earth. Not only may it live, but it also partakes of those chief accompani-

ments of life, viz., health, sickness and death. A healthy soil may, from an agricultural point of view, be regarded as one capable of fulfilling all its vital functions; a sick soil, one in which some functions are impaired. Of only one class of soil sickness may I speak, namely, that which results in producing sick plants by harboring pathogenic germs. The cotton wilt, the Texas root rot, the watermelon, tobacco, tomato and cabbage wilts, the cabbage club foot and the onion smut are conspicuous examples of diseases so propagated. Diseases of this type not only destroy the crop, but they preclude the possibility of successful culture of the plant in question, or of its close botanical relatives for many years. Such foes to agriculture have completely destroyed the possibility of tobacco growing on many farms otherwise eminently adapted to this crop and ill adapted to any other, resulting in great depreciation in the value of the land. This encroachment upon valuable soil will proceed yearly, and with geometrically increasing rapidity, until means of prevention are discovered, as they have now been in some instances, and the method of prevention becomes common knowledge. Soil diseases, the most dreaded of all dangers to the plant, are prevalent to much greater extent in the south than in the north. One field is known to exist in South Carolina upon which neither melons, cotton nor cow-peas can be grown. It is conceivable that many other germs could infest one and the same field, but no greater affliction concerning such staple crops seems possible.

Growth in popular appreciation of the importance of plant diseases and of the value of remedial and prophylactic measures is perhaps the most striking characteristic of plant pathology in the last twenty years. At the beginning of this period spraying was in no wise general. It was of rare occurrence. Man suffered unresistingly the attacks of the molds, mildews, rots and blights. The circulation of thousands of state experiment station bulletins and similar bulletins from

the national department of agriculture, the vigorous campaign of farmers' institutes, farmers' reading circles, farmers' extension courses, and the extended use of farmers' periodicals and agricultural papers have served to bring the latest discoveries of science to the use of him who will heed. As is to be expected, it is the man who most closely studies his business, he who has most at stake, the large specialist in the culture of any crop, who first embraces the offered aid. The orchardist or vineyardist leads the way in the adoption of new methods and new machinery. The revolution looking toward recognition of the value of plant treatment is now so thoroughly inaugurated that the treatment of such diseases, both insect and fungous, in the case of fruit and trucking crops is of general occurrence. The movement, too, is world-wide.

The practical outcome of all the investigation and propaganda up to the present time is that many hundreds of plant diseases have been recognized; for a hundred or more have been prescribed remedial or preventive measures, many of which are eminently successful; witness, the treatment of cereal smuts, the peach curl, the grape black rot, the powdery mildews. The saving occasioned by any one of these, as is true of scores of others, would amply suffice to pay all the expense of investigation and propaganda incurred in the development of the whole field of plant pathology. By oat smut alone the estimated damage in the United States yearly is $26,766,166, a loss avoidable by an annual expenditure of less than four cents an acre. The saving actually made in Dakota, Minnesota and Wisconsin in one year is placed at $5,000,000.

The future problems of plant pathology are manifold. The period of growth must continue long before the work now undertaken is done. Many diseases of even the cultivated plants are not yet recognized. The diseases of wild plants, particularly the weeds, must too be studied to ascertain the possibility of intercommunication of diseases between

weeds and crop plants. The life histories of all disease producing fungi must be closely studied, particularly to determine their hibernating condition. As yet the merest beginning has been made. The interrelation of host and parasite must be studied, the periods, points and modes of infection made known. The biology of the fungi, their life habits, conditions of spore formation, characters of growth, relation to light, heat, moisture, nutriment, etc.; their resistance to adverse conditions, their longevity under various conditions of environment are all problems of ultimate practicality. The question of species is unsettled and the recent demonstration of biologic varieties among the rusts, mildews and fusariums opens a large and important field of research. The agencies operating as disease distributors, the wind, insects, soil, man, water or what not must be known that such distribution be more readily controlled. The causes of resistance and susceptibility to certain diseases rest in obscurity, except in a few cases where the responsibility has been fixed upon some particular structure or chemical. The breeding of plants resistant to specific diseases not readily amenable to other means of control must proceed. Such work is now in progress with cotton, melons, tomatoes, tobacco, grains, flax and other plants. The relation existing between many root fungi and bacteria and the roots they inhabit remains to be studied. Aside from parasitism there is also mutualism, a kind of beneficial disease falling to the province of plant pathology. It needs much further study.

Specific problems also abound, the peach yellows and rosette, the mycoplasm theory of rusts, the grape Brunnisure. Differences of opinion now exist or the technique or scientific data are insufficient for an adequate solution of these questions and many other similar ones. Work on timber protection, while not strictly a question of disease, but rather a post-mortem problem, falls to the lot of the pathologist for the want of a more appropriate place. That intensive study

of a disease, however thoroughly it may seem to have been studied before, may lead to important development is well illustrated in the case of the familiar pear blight, which, though known for ages and the topic of masterly classic research, has recently, under trained observation and critical interpretation and experimentation, revealed new secrets leading to more masterful and complete control. The large fields of plant pathology, grouped under the term 'physiological disorders,' are still practically unworked; diseases due to false nutrition, absorption or assimilation, or to impaired carbon assimilation owing to improper environment, to crowding or shading or to hereditary inabilities. A start has been made sufficient to show the importance of the results awaiting.

The recent discovery of the ultramicroscopic organisms or filterable enzymes which has robbed the bacteria of the distinctioin of being the smallest of living things opens a new field in both plant and animal pathology comparable in kind, though probably not in magnitude, with the creation of bacteriology by Pasteur. It is yet unknown whether we have to do here with organisms or enzymes, and contemplation of the problems awaiting in this realm places us in a position to appreciate more fully than ever before the great controversy of spontaneous generation as fought in the sixties. The announcement in a recent periodical of the discovery of soluble protoplasm emphasizes the existence of a vast unknown covered by the words protoplasm, enzymes, invisible organisms. Is it coincidence of fate that with the growing importance of the problem of the invisible organism there comes the invention of a microscope of surpassing excellence with which the seeing of molecules is a hoped for possibility?

The science of plant pathology is indeed young. It has yielded much, and it is still full of promise. In the achievement of the results to come draught will be made upon the sister sciences even more than in the past. Plant physiology

waits upon chemistry; plant pathology upon plant physiology, and chemistry in return receives valuable contribution from both. Mathematics, physics and geology all contribute to the general upbuilding. The sciences, though becoming more divergent instead of becoming more independent, are yearly becoming more dependent, each using the discoveries of the others to gain new foothold or new tools in the search for truth. Often it is the frontier territory lying between two sciences which, belonging distinctively to neither, is least worked, and therefore presents most promising territory for conquest. Such is the history of the comparatively new sciences of physical chemistry, physiological chemistry and biometrics.

Nor does the field belong exclusively to either the devotee of pure science, so-called, or of applied science. The study of problems seemingly most remote from any practical ends has often proved fundamental in the upbuilding of vast industrial growth. Bacteriology was born of crystallography. The father of galvanic electricity was derided as the frog's dancing master. Nor does the avowed object in view give a sure key to the ultimate outcome. Alchemy, though never attaining the end sought, hastened immeasurably the era of industrial chemistry. Nor may it be said that applied science is inferior, for without the application the fundamental principles are of no avail in the promotion of the welfare of man.

Intensive laboratory study with no object other than the increase of knowledge of molecular construction has led to the commercial production of many important compounds. The present oat smut treatment by formalin owes its practicability equally to pure science in the chemical study that rendered the production of formalin practicable at moderate cost, and to pure science of the botanist who from mere interest in fungous growth discovered the nature of parasitism, and to the practical scientist who applied the knowledge of the chemist and the botanist to the solution of a

definite agricultural problem. The distinction between pure science and applied science is invidious. It is not a difference based upon the nature of the knowledge; rather upon the motive of the worker. All true science is practical, either remotely or directly, and the man of applied science is but completing the work of the pure scientist. Especially does the future of plant pathology rest with both.

A MEMOIR ON THE TWENTY-SEVEN LINES UPON A CUBIC SURFACE.

ARCHIBALD HENDERSON, PH.D.

HISTORICAL SUMMARY.

Although it is probably true that the classification of cubic surfaces is practically complete, the number of articles yearly appearing upon these surfaces furnish abundant proof of the fact that they possess much the same fascination as they did in the days of the discovery of the twenty-seven lines upon the general cubic surface. The literature of the subject is very extensive and in a bibliography* on curves and surfaces, compiled by J. E. Hill, of Columbia University, the section on cubic surfaces contained 205 articles.

The first paper that deals specifically with the cubic surface is one by L. Mossbrugger,† "Untersuchungen über die geometrische Bedeutung der constanten Coefficienten in den allgemeinen Gleichungen der Flächen des zweiten und dritten Grades," which appeared in the first volume of the *Archiv der Mathematik und Physik*, 1841.

The theory of straight lines upon a cubic surface was first studied in a correspondence by the English mathematicians Salmon and Cayley and the results were published, *Camb. and Dublin Math. Journal*, Vol. IV. (1849), pp. 118-132 (Cayley), pp. 252-260 (Salmon). The observation that a definite number of straight lines must lie on the surface is initially due to Cayley, whereas the determination of that number was first made by Salmon.‡

*Bull. Am. Math. Soc. Vol. III. (1897) pp. 136-146.

†J. E. Hill, l. c.

‡Salmon, Geom. of Three Dimensions, 4th edition, §580, note. Cf. also Cayley, Coll. Math. Papers, Vol. I., note p. 589.

The basis for a purely geometric theory of cubic surfaces was laid by Steiner* in a short but extremely fruitful memoir, containing many theorems, given either wholly without proof or with but the barest indication of the method of derivation—a habit of "*ce celebre sphinx*," as he has been styled by Cremona.

On account of the "complicated and many-sided symmetry" among the relations between the twenty-seven lines upon the cubic surface, great difficulty was at first experienced in obtaining any adequate conception of the complete configuration. The notation first given by Cayley was obtained by starting from some arrangement that was not unique, but one of a system of several like arrangements, yet it was so complicated as scarcely to be considered as at all putting in evidence the relations of the lines and triple tangent planes. Hart gave a very elegant and symmetrical notation for the lines and planes, an account of which is to be found in the original paper of Salmon,‡ who also gave a notation of limited usefulness. Schläfli‖ it was who invented the notation that might be called epoch-making—that of the double-six,‖ which has remained unimproved upon up to the present time. This notation is one out of a possible thirty-six of like character among the twenty-seven lines. Taylor† has recently given a notation for the lines independent of any particular, initial choice but this cannot be regarded as an improvement upon the Schläfli notation.

The foundations for subsequent analytic investigations concerning the twenty-seven lines were laid, as has been seen, by Cayley and Salmon, and in fact Sylvester§ once said in

*"Ueber die Flächen dritten Grades," read to the Berlin Academy, 31st January, 1856; Crelle, Bd. LIII.

‡Infra, §4.

‖Quarterly Journal, Vol. 2 (1858), pp. 55-65, 110-120.

‖For the history of the double-six theorem see infra, §6.

†Philos. Trans. Royal Soc. Vol. CLXXXV. (1894), part I. (A), pp. 37-69.

§Proc. London Math. Soc. Vol. 2, p. 155.

his habitually florid style, "Surely with as good reason as had Archimedes to have the cylinder, cone and sphere engraved on his tombstone might our distinguished countrymen leave testamentary directions for the cubic eikosiheptagram to be engraved on theirs."

The first significant papers on cubic surfaces from the synthetic standpoint, after Steiner's memoir above mentioned, were by Cremona and Rudolf Sturm. These were two of the four papers submitted in competition for the prize offered by Steiner through the Royal Academy of Sciences of Berlin in 1864, which was divided between Cremona and Sturm on Leibniz Day, 1866. The beauty and simplicity of many of the methods employed in these papers eminently justified Steiner's original remark, "Es ist daraus zu sehen, dass diese Flächen fortan fast eben so leicht und einlässlich zu behandeln sind, als bisher die Fläche zweiten Grades." Cremona's "Mémoire de géométrie pure sur les surfaces du troisieme ordre" is found in Crelle's Journal,* whereas Sturm's paper was subsequently expanded into a treatise.†

Schläfli (*l. c.*) first considered a division of the general surface of the third order into species, in regard to the reality of the twenty-seven lines, but he then contented himself with a mere survey of the problem. This was in 1858. But in 1862, F. August‡ gave a rather extended investigation of the subject. In 1863 appeared a valuable memoir by Schläfli,§ treating the subject in great detail. He also, as the title indicates, makes there a division of the surface into types, depending upon the nature of the singularities,—a classifica-

*Vol. LXVIII. (1868), pp. 1-133.

†"Synthetishe Untersuchungen über Flächen dritter Ordnung." B. G. Teubner, Leipzig, 1867.

‡"Disquisitiones de superficiebus tertii ordinis," Dissert. inaug. Berolini, 1863.

§"On the Distribution of Surfaces of the Third Order into Species, in reference to the presence or absence of Singular Points and the reality of their Lines," Philos. Trans. Vol. CLIII. (1863), pp. 193-241.

tion used by Cayley* in his "Memoir on Cubic Surfaces."

If Cayley and Salmon had wished to follow Sylvester's advice and to insert a clause in their wills, directing that a figure of the cubic eikosiheptagram be engraved upon their monuments, they would have had no certainty of the correct fulfilment of their directions until the year 1869 when Dr. Christian Wiener‡ made a model of a cubic surface, showing twenty-seven real lines lying upon it. This achievement of Dr. Wiener, Sylvester℘ once remarked, is one of the discoveries "which must forever make 1869 stand out in the Fasti of Science." Since that time, there have been constructed models of all the various types of the cubic surface, showing the lines lying entirely upon them. The list of those who have written on the mechanical construction of the configurations of the lines upon a cubic surface and the general subject of the collocation of the lines upon the surface includes the names of Salmon, Sylvester, Cayley, P. Frost, Zeuthen and Blythe.‖

The configuration of the twenty-seven lines is not only of the highest interest *per se*, but also on account of its close association and relation to other remarkable configurations. It was also in the year 1869 that Geiser§ showed the mutual interdependence of the configurations of the twenty-eight bitangents to a plane quartic curve and the twenty-seven lines upon a cubic surface, and the method of derivation of each from the other. By making use of Geiser's results, Zeuthen† obtained a new demonstration of the theorems of Schläfli†† upon the reality of the lines and tripletangent planes

*Philos. Trans. Royal Soc. London, Vol. CLIX. (1869), pp. 231-326.

‡Cf. Cayley, Trans. Camb. Philos. Soc. Vol. XII. Part I (1873), pp. 366-388, where a description of the model is given.

℘Proc. London Math. Soc. Vol. 2, p. 155.

‖Cf. infra, §§18-21.

§Math. Ann. Bd. I. (1869), pp. 129-138.

†Math. Ann. Bd. 7 (1874), pp. 410-432.

††Quarterly Journal, Vol. 2, (1858); Philos. Trans. Vol. 153 (1863).

of a cubic surface. Indeed, it is feasible to derive the properties of one configuration from the known properties of the other.*

In 1877 Cremona‡ first showed that the Pascalian configuration might be derived from the configuration of the twenty-one lines upon the surface of the third degree with one conical point (Species II., Cayley's enumeration) by projection from the conical point.

The theory of *varieties* of the third order, that is to say, curved geometric forms of three dimensions contained in a space of four dimensions, has been the subject of a profound memoir by Corrado Segre.ᵽ The depth of this paper is evinced by the fact that a large proportion of the propositions upon the plane quartic and its bitangents, Pascal's theorem, the cubic surface and its twenty-seven straight lines, Kummer's surface and its configuration of sixteen singular points and planes, and on the connection between these figures are derivable from propositions relating to Segre's cubic variety, and the figure of six points or spaces from which it springs.† Other investigators on this beautiful and important locus in space of four dimensions and some of its consequences are Castelnuovo and Richmond.§

The problem of the twenty-seven lines is full of interest from the group theoretic standpoint. In 1869 Camille Jordan‖ first proved that the group of the problem of the trisection of hyperelliptic functions of the first order is isomorphic with

*Crelle's Journal, Vol. 122 (1900), pp. 209-226.

‡Reale Accademia dei Lincei, Anno CCLXXIV. (1876-77). Roma. Also cf. infra, §§47, 48.

ᵽAtti d. R. Accad. di Scienze di Torina, Vol. XXII. (1887), pp. 547-557. Memorie d. R. Accad. di Scienze di Torino, Series 2, Vol. XXXIX. (1889), pp. 3-48.

†Richmond, Quarterly Journal, Vol. XXXIV. No. 2 (1902), pp. 117-154.

§Cf. Richmond l. c. for references.

‖Comptes Rendus, 1869. Cf. also Traite des Substitutions, p. 216 et seq., p. 365 et seq.

the group of the equation of the twenty-seventh degree, on which the twenty-seven lines of the general surface of the third degree depend. Felix Klein† in 1887 sketched the effective reduction of the one problem to the other. In 1887-9 Maschke‡ in a series of papers set up the complete form-system of a quaternary group of 51840 substitutions, and in 1893 Burkhardt,‖ on the basis of Klein's paper above mentioned, these papers of Maschke and one by Witting,§ carried out the work sketched by Klein—the reduction of one problem to the other.

Since Jordan's first paper appeared in 1869, a number of writers have studied the Galois group of the equation of the twenty-seven lines. Dickson** has led in this investigation, publishing a number of papers on the subject. Other writers on the same subject are Kühnen,†† Weber,‡‡ Cartan and, more recently, Kasner. This last paper is in close contact with the investigations of Moore and Slaught on the cross-ratio group of Cremona transformations.

INTRODUCTION.

The problem of the twenty-seven lines upon a cubic surface is of such scope and extent and is allied to so many other problems of importance that to give a *resume* of all that has

†Extrait d'une lettre addressee a M. C. Jordan, Journal de Liouville, series 4, tome IV. (1888), p. 169 et seq.

‡Math. Ann. Bd. XXX. (1887), pp. 496-515; Gött. Nach. (1888), pp. 76-86; Math. Ann. Bd. 33, (1889), pp. 317-344.

‖Math. Ann. Bd. 41 (1893), pp. 309-343.

§Math. Ann. Bd. 29 (1887).

**Trans. Am. Math. Soc. Vol. 2 (1901), pp. 137-138; Quarterly Journal Vol. 33 (1901), pp. 145-173; Bulletin Am. Math. Soc. Vol. 8 (1901), p. 63 et seq.; Linear Groups Ch. XIV. pp. 303-307.

††"Uber die Galois'che Gruppe der Gleichung 27 Grades, von welcher die Geraden auf der allgemeinen Fläche dritter Ordnung abhängen," Diss. Marburg, 1888.

‡‡Math. Ann. Bd. XXIII., pp. 489-503.

been done upon the subject would enlarge the present paper into a book. It was found impossible to cover even the geometrical phases of the problem, in their extension in particular to the cognate problem of the forty-five triple tangent planes, although the two subjects go hand in hand. In this memoir, however, is given a general survey of the problem of the twenty-seven lines, from the geometric standpoint, with special attention to salient features, i. e., the concept of trihedral pairs, the configuration of the double-six, the solution of the problem of constructing models of a double-six and of the configurations of the lines upon the twenty-one types of the cubic surface, the derivation of the Pascalian configuration from that of the lines upon the cubic surface with one conical point, and certain allied problems.

In §§ 1-4 are given certain preliminary theorems concerning the existence and number of the twenty-seven lines and forty-five planes for the general cubic surface, and upon the first notation employed. In §§ 5, 6 and 7 are given an account of Schläfli's notation, a history of the double-six theorem and an analytic proof of it, independent of cubic surfaces; in §8 follow certain interesting results on the anharmonic ratios of the configurations. In §9 appear two conditions that five lines lie upon a cubic surface and in §10 is the description of the formation, and the tabulation of the thirty-six double-sixes. In §11 occur certain auxiliary theorems for special features of the general configuration of the twenty-seven lines.

In §12 are given the definition and number of trihedral pairs, and in §13 the actual formation of the tables of the 120 forms. In §14 these are grouped together in such a way (sets of three) as to determine in forty ways all the twenty-seven lines.

In §16 is given a discussion of a special form of the general equation of the cubic surface and the determination of the equations of the forty-five triple tangent planes.

In §§18 and 19 the methods for the construction of a model

of a double-six are discussed and a practical method is there given in detail.

In §§20 to 45 the general problem of constructing thread or wire models of the configurations of the lines upon all twenty-one types of the cubic surface is fully considered, and a complete solution of the problem given.

In §46 is given a discussion of the derivation of the Brianchon configuration from two spatial point triads, and in §§47-8 the discussion of the derivation of the Pascalian configuration from that of the straight lines upon the second species of the cubic surface (Cayley's enumeration) and a graphic representation of the same.

Finally, in §49 appears a theorem on the number of cubic surfaces with one conical point passing through the lines of mutual intersection of two triheders.

CHAPTER I.

PRELIMINARY THEOREMS.

§1 *Existence of Straight Lines upon a Cubic Surface.*

In order to find the conditions that any straight line, whose equations are

$$\frac{x - x_0}{\lambda} = \frac{y - y_0}{\mu} = \frac{z - z_0}{\nu} = r,$$

lie entirely upon a surface, we substitute $x = x_0 + \lambda r$, $y = y_0 + \mu r$, $z = z_0 + \nu$ in the equation of the surface, arrange the terms of the resulting equation according to powers of r and then set all the coefficients of r equal to zero,

since the equation in r must be identically satisfied, i. e., for all values of r. Since in this case the equation of the surface is of the third degree, there result four conditions. But the equations of a straight line involve four disposable constants, and, as the number of conditions to be fulfilled is exactly equal to the number of disposable constants in the equations of the straight line, it follows that every surface of the third order must contain a finite number of straight lines, real or imaginary, lying entirely upon it.

§2. *Number of Straight Lines upon a Cubic Surface.*

Suppose we pass a plane π through a point P outside the surface and through a straight line l lying upon the surface. Then π meets the surface in the line l, and a conic C besides (since the curve of intersection is a degenerate cubic), i. e. meets the surface in a section having two double-points and therefore by definition is a double-tangent plane. These double-tangent planes π to the cubic surface are also double-tangent planes to the tangent cone, vertex P. Now since to every plane π corresponds one straight line l lying entirely on the surface and as there are twenty-seven* ($n = 3$) double-tangent planes to the tangent cone, vertex P, therefore there are twenty-seven straight lines l on the cubic surface.†

§3. *Triple Tangent Planes.*

By properly determining the plane passed through any straight line l upon the cubic surface, the conic C (§2) will

*Salmon, Geom. of Three Dimensions, 4th edition, §286 gives

$$\frac{n}{2}(n-1)(n-2)(n^3-n^2+n-12)$$

as the number of double-tangent planes, drawn through a point P to a surface of the nth degree.

†For other proofs compare R. Sturm, Flächen dritter Ordnung, Kap. 2, §20, and Cayley, Coll. Math. Papers, Vol. I., No. 76 (445-456).

degenerate into a pair of straight lines. Here the plane intersects the surface in three intersecting straight lines (a degenerate curve of the third order having three double points) and the points of intersection of the lines taken in pairs are the points of contact of the plane with the surface. Now through each of the three lines in the plane there may be drawn, besides the given plane, four triple tangent planes. For these twelve new planes give rise to twenty-four new lines upon the surface, making up with the former three lines, twenty-seven lines upon the surface. It follows that every straight line on the surface is met by ten others.

If all the twenty-seven lines intersect in pairs, there would be 351 points of intersection. But since each line is met by ten other lines, there remain 16 lines by which it is not met and therefore there are $\frac{27 \times 16}{2} = 216$ pairs of lines that do not intersect. Consequently there are 135 points of intersection.

Since these 135 points, by threes, determined the triple tangent planes, there are 45 triple tangent planes.

Consider the three lines a, b, and c say, the complete intersection of the triple tangent plane π with the surface. Then every other line l upon the surface must meet the triple tangent plane in a point upon one (a say) of the three lines a, b, and c, and accordingly must lie in a plane π_l, passing through a. Since the intersection of the surface by the plane π_l must be a cubic curve, which is already composed of two straight lines, the plane π_l meets the surface in a third straight line l', and therefore must be a triple tangent plane. Hence l' must be one of the given 27 lines and it appears that there can be but 27 lines upon a cubic surface.

§4. *Salmon's Notation for the Twenty-Seven Lines.**

Lemma. *The general equation of the cubic surface may be*

*Camb. and Dublin Math. Journal (1849), Vol. IV., pp. 252-260.

reduced to the canonical form $uvw - \xi\eta\zeta = 0$, *where* u, v, w, ξ, η, ζ *are linear polynomes.*

The number of independent constants in the general equation of the third degree is $19\left[\frac{n\,(n^2 + 6n + 11)}{6}, \text{ for } n = 3\right]$. Since the linear polynomes u, v, w, ξ, η, ζ contain 18 ratios of coefficients and there is one other constant factor implicitly contained in one of the products uvw, $\xi\eta\zeta$, therefore the forms $uvw - \xi\eta\zeta = 0$ contains 19 constants and is one into which the general equation of a cubic surface may be thrown.

It will appear later (§15) from geometrical considerations that the problem to reduce the base cubic to the form $uvw - \xi\eta\zeta = 0$ is soluble in 120 different ways.

NOTATION. Consider the canonical form of the surface of the third degree $ace - bdf = 0$, where a, b, c, d, e, f are linear polynomes. By inspection it is patent that this surface contains the nine lines ab, ad, af, cb, cd, cf, eb, ed, ef where ab, for example, represents the line of intersection of the planes $a = 0$, $b = 0$. If we suppose $a = \mu b$ to be the equation of one of the triple tangent planes through the intersection of the planes a and b, the plane $a = \mu b$ meets the surface in the same lines in which it meets the hyperboloid $\mu ce - df = 0$, that is, the two lines in the plane are generating lines of different species, and consequently one of them meets the pair of lines cd and ef, and the other of them meets the pair of lines cf and ed. Let us now denote each of the remaining eighteen lines by the three lines which it meets, the line meeting ab, cd and ef being denoted by the symbol $ab \cdot cd \cdot ef$. Since μ has three values, there are three lines that meet ab, cd, ef. Applying the same reasoning to the planes through bc and ca, we employ the following symbolism for the twenty-seven lines ab, ad, - - - - - ef; $(ab \cdot cd \cdot ef)_i$, $(ad \cdot cf \cdot eb)_i$, $(af \cdot cb \cdot ed)_i$, $(ab \cdot cf \cdot ed)_i$, $(ad \cdot cb \cdot ef)_i$, $(af \cdot cd \cdot eb)_i$, where $i = 1, 2, 3$.

Unfortunately our information as to how these suffixes are to be applied is inadequate and certain postulates have to be made as to how the intersections occur.* This notation of Salmon was the first one that was given for the twenty-seven lines, and was superseded by a very superior one to be explained in the next article.

*Cf. Salmon, l. c.

MOLECULAR ATTRACTION, IV., ON BIOT'S FORMULA FOR VAPOR PRESSURE AND SOME RELATIONS AT THE CRITICAL TEMPERATURE.[1]

J. E. MILLS.

THE $\frac{\delta P}{\delta T}$ OF A LIQUID.

In a preceding paper[2] we examined the following equation, which had been proposed on theoretical grounds by Mr. H. Crompton,

$$[1] \qquad L = 2\int_v^V p\delta v = 2RT\log_e \frac{d}{D} = \frac{9.154}{m} T \log \frac{d}{D} \text{ cals.}$$

(L is heat of vaporization, v and V denote volume of liquid and vapor, d and D the density of liquid and vapor, p is pressure, T is temperature, m is molecular weight, R is the constant of the gas equation, $PV = RT$.)

It was there shown that this equation gives at low temperatures where the pressure is small, results for the heat of vaporization that are invariably and usually very considerably too large. But at the higher temperatures examined, that is as the critical temperature is approached, the results given by the equation appeared to be correct. The evidence there given as to the correctness of this equation at high temperatures was very considerable and justified further use of the equation. Therefore in this paper we combined the usual thermodynamical equation for calculation of the heat of vaporization,

[1]Reprinted, with omission of a Table, from Jour. Phys. Chem., 9, p. 402, 1905.

[2]Jour. Phys. Chem. 8, 593 (1904).

$$[2] \qquad L = \frac{T}{J}(V - v)\frac{\delta P}{\delta T} = .0_{4}31833\, T\,(V - v)\frac{\delta P}{\delta T} \text{ cals.}$$

with the equation of Crompton given above, and obtained equation 15 of that paper, viz.:

$$[3] \qquad \frac{\delta P}{\delta T} = \frac{287500}{m}\frac{\log \frac{V}{v}}{V - v}$$

We there showed that the limit approached by this equation as the critical temperature was approached and V approached v in value, was,

$$[4] \qquad \frac{\delta P}{\delta T} = \frac{124860}{mV}.$$

We at that time overlooked the fact that this equation 4 could be expressed in the very simple form,

$$[5] \qquad \frac{\delta P}{\delta T} = \frac{2R}{V}.$$

Here V is the critical volume and R is the usual gas constant, and we have the striking conclusion that *at the critical temperature the* $\frac{\delta P}{\delta T}$ *of the liquid (vapor) is exactly twice what it would be for that substance as a perfect gas occupying the same volume.* Expressed in this form the bearing of equation 3, or its limiting forms, on the kinetic relations of a liquid and its vapor, assumes more importance and justifies a closer study.

Accordingly by means of equation 4, we calculated, and give in Table 1, the values of the $\frac{\delta P}{\delta T}$ at the critical temperature for twenty substances. The critical data used is that given by Dr. Young[1]. This data is more correct than that given in earlier papers. (We would here note that in the third paper on Molecular Attraction[2] we overlooked this corrected data, but have since repeated the calculations there given

[1] Phil. Mag., [5], 50, 291 (1900).

[2] Jour. Phys. Chem., 8, 593, (1904).

using the corrected data and find no material change in the results or conclusions there expressed.)

For comparison with these values the $\frac{\delta P}{\delta T}$ can be calculated from any equation connecting vapor pressure and temperature. Of the numerous equations that have been proposed the one usually known as Biot's has proved by far the most serviceable. It takes the form,

[6] $$\text{Log } P = a + b \cdot \alpha^t + c \cdot \beta^t.$$

By differentiating and changing to Naperian logarithms we get,

[7] $$\frac{\delta P}{\delta T} = 5.3019\, P(b \cdot \log \alpha \cdot \alpha^t + c \cdot \log \beta \cdot \beta^t).$$

Since we had previously used Biot's formula for calculating heats of vaporization more directly, we found it easier to throw equation 7 into the form,

[8] $$\frac{\delta P}{\delta T} = .031414\, P\, A,$$

where, $A = 168.775\,(b \cdot \log \alpha \cdot \alpha^t + c \log \beta \cdot \beta^t)$. The constants for this equation have already been given[1] for all of the substances examined except those noted below.

Ethyl oxide. $A = \text{antilog } (\bar{1}.9882227 - .00172541\, t) + \text{antilog } (\bar{1}.7399799 - .00869664\,)$, $t = t°$ C.

Benzene. $A = \text{antilog } (\bar{1}.4256719 + .0001302029\, t) + \text{antilog } (0.1799122 - .00410411\, t)$, $t = t°$ C.

Methyl alcohol. $A = \text{antilog } (\bar{1}.5561254 - .00011584\, t) + \text{antilog } (.2.51667 - .00400204\, t)$, $t = t°$ C.

Ethyl alcohol. $A = \text{antilog } (\bar{2}.3965216 + .003377538\, t) + \text{antilog } (0.3342413 - .00317576\, t)$, $t = t°$ C.

[1] Jour. Phys. Chem., 8, 388 (1904).

Propyl alcohol. $A = \text{antilog } (\bar{2}.8340346 + .001641423\,t) + \text{antilog } (.03135244 - .00342975\,t)$, $t = t^\circ\,C - 20$.

The constants for ethyl formate and methyl acetate were kindly sent me by Dr. Young (work yet unpublished) and the constants for methyl formate I have calculated and will publish later.

The values of the $\frac{\delta P}{\delta T}$ at the critical temperature as obtained from these Biot equations are shown in Table 1.

Of the twenty substances compared in Table 1 it will be seen that the $\frac{\delta P}{\delta T}$ from equation 4 has a higher value than the $\frac{\delta P}{\delta T}$ calculated from Biot's formula in all cases except di-isobutyl, normal octane, and ethyl alcohol. The difference is usually very marked.

In work done upon an equation of the form, $P = bT - a$, Ramsay and Young[1] made a study of the $\frac{\delta P}{\delta T}$ of ether at constant volume, Young[2], later, a similar study for isopentane, and Rose-Innes and Young[3] corresondingly for normal pentane. At the critical volume the values of the $\frac{\delta P}{\delta T}$ obtained at constant volume becomes identical with the value of the $\frac{\delta P}{\delta T}$ denoting the increase in vapor pressure of the liquid. Therefore it is possible in these three cases by comparison with the values of the $\frac{\delta P}{\delta T}$ obtained in the above papers to determine whether the values of the $\frac{\delta P}{\delta T}$ calculated from Biot's

[1] Phil. Mag. [5], **23**, 435, (1887).
[2] Ibid, [5], **38**, 569, (1894).
[3] Ibid. [5], **47**, 353 (1899).

TABLE 1.

SUBSTANCE	Critical Temperature	$\frac{\delta P}{\delta T}$ from Equation 4	$\frac{\delta P}{\delta T}$ from Biot	Δ	A
Ethyl oxide	194.45°C	441.9	391.6	50.3	.46068
Di-isopropyl	227.35	349.6	321.0	28.6	.43795
Di-isobutyl	276.8	258.8	261.6	—2.8	.44672
Isopentane	187.8	405 7	367.8	37.9	.46822
Normal pentane	197.2	402.3	364.8	37.5	.46331
Normal hexane	234.8	339.9	315.9	24.0	.44826
Normal heptane	266.85	291.9	286.9	5.0	.44782
Normal octane	296.2	254.5	256.8	—2 3	.43647
Benzene	288.5	487.0	445.4	41.6	.38961
Hexamethylene	279.95	406.0	376.0	30.0	.39583
Fluo-benzene	286.55	460.1	430.7	29.4	.40428
Carbon tetrachloride	283.15	452.7	416.7	36.0	.38808
Stannic chloride	318.7	355.2	332.5	22.7	.37689
Methyl formate	214.0	725.6	619.2	106.4	.43872
Ethyl formate	235.3	545.0	479.7	65.3	.43091
Methyl acetate	232.7	548.3	502.3	46.0	.45454
Methyl alcohol	240.0	1061.1	971.1	90.0	.51729
Ethyl alcohol	243.1	747.0	796.7	—49.7	.52998
Propyl alcohol	263.7	568.3	562.4	5.9	.47181
Acetic acid	321.65	729.2	574.6	154.6	.42066

formula or those obtained from equation 4 are correct. The result is shown below, the value of the $\frac{\delta P}{\delta T}$ at the exact critical volume having been obtained from the above mentioned papers by interpolation and entered in the column marked "Observed".

Substance	Volume	From Biot	Equ'tion 4	Observed
Ether	3.815	391.6	441.9	436
Isopentane	4.268	367.8	405.7	401 to 411
Normal pentane	3.305	364.8	402.3	406.7

In every case the values accord to within the limit of experimental error with the values derived from Biot's equation. (It is not possible to extend the comparison to the alcohols and acetic acid studied by the observers above mentioned, for these liquids are associated and equation 4 depending on the molecular weight, could not give correct results.

ON BIOT'S FORMULA FOR VAPOR PRESSURE.

It seemed to us reasonable to conclude from the above comparison that the ratios of the $\frac{\delta P}{\delta T}$ calculated from equation 4 at the critical temperature and shown in Table 1 were the correct values and that the values obtained from Biot's formula were in error. Fortunately we had a means of verifying this conclusion directly.

If the vapor pressure curve be plotted, the $\frac{\delta P}{\delta T}$ is the tangent to the curve. Assuming that Biot's formula does correctly represent the vapor pressures until the critical temperature is approached (an assumption justified by a very careful examination of the curves over the entire range of temperature) it is evident that if the $\frac{\delta P}{\delta T}$ calculated from Biot's form-

ula then becomes too low it must be because the vapor pressure curve as calculated from Biot's formula is below the true vapor pressure curve. We accordingly subtracted the observed vapor pressures from the calculated in the immediate neighborhood of the critical temperature. (These results are shown in detail in Table 2, Jour. Phys. Chem. 9, p. 402 [1905]). In every case except normal octane, stannic chloride, and the associated substances (methyl alcohol, ethyl alcohol, and acetic acid), the calculated minus the observed vapor pressures does give negative differences at the highest temperature compared (usually the critical temperature itself). With regard to these five exceptions, the associated substances cannot give exactly correct results by the use of equation 4 and their evidence does not therefore bear upon that equation. Normal octane and stannic chloride are the only substances whose divergence can be considered as evidence against the conclusion above derived and it is sufficient to point out in explanation a remark made by Dr. Young[1] when the vapor pressures of normal octane were published. He there states that the observed values of the vapor pressure above 280° C for *normal octane*, *stannic chloride*, *and acetic acid*, are probably *too low* owing to an error in the temperature scale, i. e., in the boiling points of the liquids used as a heating jacket.

A close examination of the observed and calculated vapor pressure curves reveals the fact that no matter how the constants for Biot's formula be altered they cannot exactly represent the true vapor pressures in the neighborhood of the critical temperature. The deviation is very slight, usually negligible when the vapor pressure is considered, because the proportional error is very small. But when the $\frac{\delta P}{\delta T}$ is considered the proportional error is very large.

Since Biot's formula was empirical and in the immediate neighborhood of the critical temperature was forced to fit a curve it could not exactly follow it usually happens that the

[1] Jour. Chem. Soc., 77, 1147 (1900).

TABLE 2.

SUBSTANCE	Temperature	Old μ'	New μ'	Mean μ'	Critical Temperature	μ' From Equation 12	$\frac{P V m}{T}$
Ethyl oxide	193	90.7	102.0	104.4	194.4	102.1	16360
Di-isopropyl	225	92.0	96.8	98.1	227.4	96.5	16660
Di-isobutyl	274	86.4	82.3	86.3	276.8	80.7	16370
Isopentane	187.4	99.3	107.0	105.4	187.8	107.0	16710
Normal pentane	197	98.8	109.9	109.9	197.2	109.4	16570
Normal hexane	234	94.2	99.5	102.85	234.8	99.2	16290
Normal heptane	266.5	90.8	91.0	98.75	266.9	90.8	16170
Normal octane	290	91.0	84.8	93.0	296.2	84.2	16140
Benzene	280	107.8	111.2	109.5	288.5	110.5	16610
Hexamethylene	279	98.1	104.7	103.6	280.0	104.5	16820
Fluo-benzene	280	84.7	85.75	85.6	286.55	85.2	16440
Chlor-benzene	.....	.....	.....	81.2	360.0	81.5	16490
Brom-benzene	.....	.....	.....	56.1	397.0	56.3	16380
Iodo-benzene	.....	.....	.....	44.4	448.0	43.8	16500
Carbon tetrachloride	280	43.9	45.5	44.1	283.15	45.3	16940
Stannic chloride	280	23.15	26.96	26.04	318.7	25.87	16680
Methyl formate	213.5	101.2	120.1	121.5	214.0	119.8	15910
Ethyl formate	284	94.0	104.4	107.2	235.3	103.9	16040
Methyl acetate	233	96.6	108.8	109.5	233.7	103.6	15800
Methyl alcohol	238.5	259.4	264.3	305.0	240.0	262.4	13705
Ethyl alcohol	242.5	197.2	178.9	241.2	243.1	179.9	15495
Propyl alcohol	260	157.0	144.6	199.2	263.7	143.7	15590
Acetic acid	320	116.4	150.6	.....	321.6	150.7	12502

curve of observed vapor pressures cuts the curve of calculated vapor pressures in the neighborhood of the critical temperature, the observed vapor pressure curve having, of course, the steeper trend. This is at once evident by the change from positive to negative values of the differences between the calculated and observed vapor pressures.

We would here point out the great accuracy of these measurements made by Drs. Ramsay and Young and by Dr. Young and his co-workers. The conclusion that the calculated minus the observed vapor pressure should be negative near the critical temperature was wholly theoretical on our part. That we should be able at once to verify this conclusion from the measurements when the differences were so small as to have been laid by the observers themselves on the errors of measurement (the regularity of the differences having escaped observation) speaks for itself as to their accuracy and skill. The observed and calculated vapor pressure lines are almost indistinguishable even at the critical temperature and when drawn to a large scale.

In order to show that equation 4, or the more general form equation 3, does give results in accord with Biot's formula at points considerably below the critical temperature we have published in Table 2, Jour. Phys. Chem. 9, p. 408 (1905), the values of the $\frac{\delta P}{\delta T}$ calculated from both formulas at intervals for some 50° C below the critical temperature. We have already pointed out that equation 3 itself becomes inaccurate at yet lower temperatures.

CORRECT VALUES FOR μ' NEAR THE CRITICAL TEMPERATURE.

Since equation 3 enables us to obtain in the neighborhood of the critical temperature more nearly correct values for the $\frac{\delta P}{\delta T}$ than we had been able to obtain in previous papers when

working with Biot's formula we concluded to use these values and test more thoroughly the equation,

$$[9] \qquad \frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant} = \mu'.$$

discussed in previous papers[1]. If the value of the $\frac{\delta P}{\delta T}$ from equation 3 be substituted in the thermodynamical equation 2, the values of the heat of vaporization so calculated are the same as those obtained from equation 1. Therefore using these values and substituting them in equation 9 we obtain the corrected values for the constant. The results so obtained at those points nearest the critical temperature are given in Table 2 under the heading "New". For comparison we give under heading "Old" the values that we had previously obtained for μ' at this same temperature when using the $\frac{\delta P}{\delta T}$ obtained from Biot's formula in calculating the heats of vaporization thermodynamically. Also we give, under the heading "Mean", the average value of the constant previously adopted. Agreement is not of course to be expected for the four associated substances last shown in the table. For the other substances there is little question but that the constants so obtained agree with the mean values to within the limit of experimental error except in the cases of di-isobutyl, normal heptane, normal octane, and methyl acetate. We are unable to explain the smaller values obtained from these four substances, but the proof that equation 9 does hold as near the critical temperature as it is possible for measurements to be made is now complete for ethyl oxide, di-isopropyl, isopentane, normal pontane, normal hexane, benzene, hexamethylene, fluo-benzene, carbon tetrachloride, stannic chloride, methyl formate, and ethyl formate.

[1] Jour. Phys. Chem., April, 1902; June, 1904; Dec., 1904.

THE VALUE OF μ' AT THE CRITICAL TEMPERATURE.

It is possible to extend this proof quite to the critical temperature itself. Substituting in equation 9 the value of L, given by the thermodynamical equation 2, and the value of $E_1 = .0_4 3183\, P\,(V - v)$, we have

$$[10] \qquad \frac{.0_4 31833 \left(T\frac{\delta P}{\delta T} - P\right)\left(V - v\right)}{\sqrt[3]{d} - \sqrt[3]{D}} = \mu',$$

and obtaining the limit of this equation as V approaches v in value we have for the equation at the critical temperature, where $V = v$, the form

$$[11] \qquad .0_4 955\, V^{\frac{1}{3}}\left(T\frac{\delta P}{\delta T} - P\right) = \mu'.$$

As we have shown the most correct value for the $\frac{\delta P}{\delta T}$ available at this temperature is that given by equation 4 and substituting this value in the equation we get,

$$[12] \qquad \mu' = V^{\frac{1}{3}}\left(\frac{11.924\, T}{m} - .0_4 955\, P\, V\right).$$

This equation is the same as equation 17 of the third paper[1]. Here V, T, and P, are the critical volume, temperature, and pressure respectively, and m is the molecular weight of the substance under consideration. The equation is interesting because it gives a method for calculating the constant of molecular attraction, μ', in terms of the critical constants and the molecular weight of the substance. Since the molecular weight enters into the equation it evidently cannot be applied to associated substances. Again using the critical data, already referred to, given by Young, the values obtained from this equation are shown in Table 2 above. Except for di-isobutyl, normal heptane, normal octane, methyl acetate,

[1]Jour. Phys. Chem., Dec., 1904.

and to a less degree for ethyl formate, the agreement with the mean values of μ' is excellent and we may therefore regard the truth of equation 9 as having been established at the critical temperature itself for fifteen of the nineteen substances under consideration. (Ethyl formate decomposes slightly at the higher temperatures which is sufficient to account for the divergence, three per cent., there observed.) We have already shown that normal heptane and normal octane give constant values for μ' in equation 9 over a range of more than 200° C in temperature. We have unpublished results showing the same to be true for methyl acetate. Diisobutyl did give a variation of several per cent. at low temperatures, a divergence that we think was sufficiently explained[1]. It would seem probable therefore that the divergences shown by these four substances at the critical temperature must be due to some change or decomposition taking place in the substance at that temperature and that equation 9 is applicable for all normal substances quite up to the critical temperature.

RATIO OF THE THEORETICAL TO THE ACTUAL CRITICAL DENSITY.

In a preceding paper[2] we showed that the molecular attraction at unit distance, μ, was equal to $c\mu'\sqrt[3]{m}$. Therefore we have from equation 12,

$$[13] \qquad \mu = c\sqrt[3]{m}\,\mathrm{V}\left(\frac{11.924\,\mathrm{T}}{m} - .0{,}955\,\mathrm{P\,V}\right).$$

In the same paper on the assumption that the critical temperature was the point where the kinetic energy of the molecules was just balanced by the molecular attraction we derived equation 24 of that paper, viz.:

[1] Jour Phys. Chem., 8, 595 (1904).

[2] Jour. Phys. Chem., 8, 680 (1904).

[14] $$\mu = c' \frac{T}{m \sqrt[3]{V}} \sqrt{\frac{m}{d}}.$$

where T is the critical temperature and d is the critical density. We can now combine this value of μ with the value of μ given in equation 13 and obtain,

[15] $$c' \frac{T}{m \sqrt[3]{V}} \sqrt{\frac{m}{d}} = \sqrt[3]{mV} \left(\frac{11.924\,T}{m} - .0_4955\,PV \right),$$

whence,

[16] $$\frac{PVm}{T} = \text{constant.}$$

We show the values of $\frac{PVm}{m}$ in Table 2 and it will be seen that hexamethylene and carbon tetrachloride alone (the associated substances being excepted) give a value more than three per cent. from the average value 16293.

$\frac{.0_416014\,Pm}{T}$ is the theoretical critical density and equation 16 is really the ratio of the theoretical, D_c, to the actual critical density, d_c, and can take the form,

[17] $$\frac{D_c}{d_c} = \text{constant.}$$

The relation in this form has been fully discussed by Dr. Young[1]. It here appears as a necessary consequence of the ideas that we have advanced though we did not foresee that such would be the case, and hence are justified in considering the deduction of this relation as further evidence that those fundamental ideas upon which this series of papers is based are correct.

It may seem unusual that we should have been able to derive two different equations for μ (equations 13 and 14) in terms of the critical constants. This is due to the fact that the critical temperature besides possessing the property that the molecular attraction just balances the kinetic energy of the molecules—the relation upon which equation 14 is based

[1] Phil. Mag., [5], 50, 291 (1900).

—can also be viewed as the boiling point and from this point of view permits the deduction of equation 13. We hope shortly to complete a paper applying these ideas of molecular attraction more fully to the boiling point.

We should also point out that by combining equation 11 with equation 14, we get,

$$[18] \qquad \frac{T}{m} = cV\left(T\frac{\delta P}{\delta T} - P\right),$$

where c is a constant. This equation can be solved so as to give any one of the variables at the critical temperature in terms of the others and the molecular weight. It is not feasible now to further examine this equation, since the only correct values for the $\frac{\delta P}{\delta T}$ are obtained from equation 4 and this at once reduces the equation to the form of equation 16.

Dr. Young has shown that the average constant of equation 17 is $\frac{1}{3.827}$. Since the theoretical critical pressure is therefore 3.827 times the actual critical pressure it follows from the gas law and equation 5 that at the critical temperature,

$$[19] \qquad \frac{\delta P}{\delta T} = \frac{7.654\,P}{T}.$$

This equation can be obtained directly from equation 18 but the constant is then unknown.

SUMMARY.

1. It is shown that the $\frac{\delta P}{\delta T}$ for a liquid (vapor) at the critical temperature is exactly twice what it would be for the same substance as a gas occupying the critical volume.

2. It is shown that Biot's formula for vapor pressure cannot be made exactly to fit the true vapor pressure curve in the immediate neighborhood of the critical temperature. When

the pressure is considered the proportional error is very small. When the $\frac{\delta P}{\delta T}$ is considered the proportional error is large, and the values obtained from Biot's formula are too small.

3. The equation, $\frac{L - E_1}{\sqrt[3]{d} - \sqrt[3]{D}} = \mu'$, where μ' is the constant of molecular attraction, is shown to be applicable with exactness in the immediate neighborhood of and at the critical temperature for fifteen out of nineteen substances considered. The equation has already been proved accurate at lower temperatures.

It is shown that the constant of molecular attraction, μ', can be calculated from the critical constants and the molecular weight.

5. The known fact that the ratio of the theoretical to the critical density is a constant for all substances is shown to follow necessarily from the fundamental ideas and equations upon which this series of papers is based.

University of North Carolina,
April 3rd, 1905.